
(12) **UK Patent Application** (19) **GB** (11) **2 149 392 A**

(43) Application published 12 Jun 1985

(21) Application No **8330137**

(22) Date of filing **11 Nov 1983**

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(51) INT CL⁴
C03C 23/00 25/00

(52) Domestic classification
C1M 401 LB

(56) Documents cited
None

(58) Field of search
C1M

(54) **Surface treatment of glass**

(57) Silica glass, possibly containing dopant material, for conversion into or in the form of optical fibres, possibly with a primary coating, is treated by exposure to deuterium such as to form deuteroyl groups therein prior to exposure to hydrogen, whereby the possibility of the formation of hydroxyl groups in the glass on subsequent exposure to hydrogen, is reduced.

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SPECIFICATION

Treatment of glass

5 This invention relates to the treatment of glass and in particular to a method of treating silica glass for use as optical fibres.

Optical fibres are becoming of increasing importance for use in communication systems where they are used for signal transmission in place of previously used electrical conductors. The advantages of optical over electrical signal transmission are well known and will not therefore be discussed herein.

15 Known optical fibres are made from silica glass containing boron and/or fluorine and/or phosphorus and/or germanium dopant, the fibres being drawn to a required diameter, say $125\mu\text{m}$, from a preform, using known fibre drawing techniques.

It is important that optical signals passing through an optical fibre be attenuated as little as possible by the fibre, and that any attenuation by the fibre remains substantially constant during the working life of the fibre.

25 However, it has been found that optical signal attenuation by fibres made of silica glass increases when fibres are exposed to hydrogen of natural isotopic abundancies, and surprisingly that this effect occurs under very modest conditions, for example at ambient temperature and less than one atmosphere partial pressure of hydrogen. The attenuation increases are caused by the formation of hydroxyl groups in the glass and are significant at the wavelengths of interest for long-distance optical signal transmissions, that is wavelengths between $1.2\mu\text{m}$ and $1.6\mu\text{m}$, and particularly at $1.3\mu\text{m}$ and $1.55\mu\text{m}$ wavelengths at which optical fibres commonly have minimum dispersion and minimum attenuation, respectively.

Thus, there is a requirement for silica glass with low hydroxyl content for the manufacture of optical fibres.

It is known that the extent of reaction of hydrogen with silica glass to form hydroxyl groups is dependent upon the method used to produce the silica, and silica glass with low hydroxyl group content can be made using known methods by electrical fusion of quartz, or by oxidation of silicon tetrachloride in a hydrogen-free oxygen-containing atmosphere.

However, silica made by such methods is known to be able to react with hydrogen to form a limited amount of hydroxyl groups, typically between 15 and 100 ppm (by weight). It has been speculated that the reaction occurs at defect sites in the silicate network, and that the extent of reaction is limited by the concentration of such reactive defect sites.

Thus, optical fibres produced from preforms of silica glass made by these known methods will suffer from the disadvantage that the

hydroxyl group content, and thus the optical signal attenuation, will increase if the fibres are exposed to hydrogen after manufacture.

According to this invention a method of treating silica glass, comprises exposing the glass to deuterium such as to form deuteriohydroxyl groups in the glass prior to exposure of the glass to hydrogen, and thereby reduce the possibility of the formation of hydroxyl groups in the glass on subsequent exposure of the glass to hydrogen.

The presence of deuteriohydroxyl groups in the silica glass still results in an increase in optical signal attenuation by a fibre made from the glass, but the attenuation spectrum is different, and in particular there is less attenuation increase with deuteriohydroxyl groups than with hydroxyl groups at the wavelengths of particular interest, that is at $1.3\mu\text{m}$ and $1.55\mu\text{m}$ wavelengths.

The glass may be treated at any stage of the fibre manufacturing process during, or subsequent to, the preform production stage. The treatment conditions must be chosen so that deuterium gas diffuses into the glass in sufficient quantity and for sufficient time so that substantially all the reactive sites in the glass are converted to deuteriohydroxyl groups. Suitable conditions may be approximately calculated from the known rates of diffusion and reaction of hydrogen isotopes in silica glass, the dimensions of the glass being treated and the time, temperature or deuterium partial pressure in which the treatment is to be performed. The approximation arises because doped glasses used for optical fibre manufacture may be expected to have somewhat different physical and chemical characteristics from those of pure silica. Some experimental treatments may therefore be required to establish the proper conditions for each particular size and composition of glass.

In order to overcome the problems of the incorporation of hydroxyl groups in silica glass fibres it has been proposed to subject preforms from which the fibres are to be drawn, or short lengths of drawn fibre, to isotopic exchange in deuterium gas at high temperature, say 100°C , such treatment resulting in deuterium atoms displacing hydrogen atoms from hydroxyl groups already present in the glass. The presence of deuteriohydroxyl groups in the glass replacing the previously present hydroxyl groups has the advantage that the optical signal attenuation of fibres made from the preforms is favourably altered, as already described.

However, the treatment of preforms with deuterium under appropriate conditions by the method of this invention has the advantage of reducing subsequent formation of hydroxyl groups on exposure to hydrogen, because reactive sites are converted to unreactive deuteriohydroxyl groups. This is quite separate from the known effect of isotopic exchange of pre-

- existing hydroxyl groups, which is in any case only advantageous for preforms or fibres which already contain an undesirable high concentration of hydroxyl groups. Also, the known method of isotope exchange treatment of silica glass has the disadvantage that if drawn fibres are treated at the high temperatures necessary for isotopic exchange they become very brittle and are thus not suitable for many practical applications.

- It is an advantage that it is possible using the method of this invention to treat the glass not only as a preform but also in fibre form, and a fibre being treated can have a primary coating, as is frequently used to preserve the strength of the fibre. This advantage is in part a consequence of the modest temperatures required for diffusion of deuterium into a fibre of small diameter in a reasonable time, and in part a consequence of the readiness of the reactive sites to form deuteroxyl groups.

CLAIMS

1. A method of treating silica glass, comprising exposing the glass to deuterium such as to form deuteroxyl groups in the glass prior to exposure of the glass to hydrogen, and thereby reduce the possibility of the formation of hydroxyl groups in the glass on subsequent exposure of the glass to hydrogen.
2. A method as claimed in claim 1, in which the glass contains boron and/or fluorine and/or phosphorus and/or germanium dopant.
3. An optical fibre made from glass treated by a method as claimed in claim 1 or claim 2.
4. A method of manufacturing an optical fibre as claimed in claim 3, in which the glass is treated when in the form of a preform from which the fibre is to be drawn.
5. A method of manufacturing an optical fibre as claimed in claim 3, in which the glass is treated when in fibre form.
6. A method as claimed in claim 5, in which the glass fibre when treated has a primary coating serving to preserve the strength of the glass fibre.